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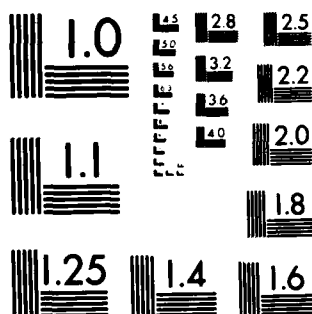
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DIELECTRIC DISPERSION IN OPTICAL ELECTRON TRANSFER IN SOLUTION

by

Paul Delahay

New York University
Department of Chemistry
New York, NY

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DIELECTRIC DISPERSION IN OPTICAL ELECTRON TRANSFER IN SOLUTION

PAUL DELAHAY

Department of Chemistry, New York University, New York, New York 10003, USA

Dielectric dispersion causes the outer-sphere reorganization free energy to vary with photon energy in optical electron transfer. The resulting distortion of the spectral response for photoelectron emission may yield misleading evidence about the emission yield vs. photon energy relationship. Dispersion is taken into account in the calculation of emission threshold energies and the correlation between optical and thermal electron transfer. Results are given for V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, $Fe(CN)_6^{4-}$.

1. INTRODUCTION

Optical electron transfer in solution can be interpreted [1] on the basis of ideas transposed from theories of thermal electron transfer [1-3]. Thus, optical electron transfer is considered to be fast in comparison with subsequent reorganization of nuclear positions. The free energy of reorganization R is equated to the sum of inner- and outer-sphere contributions, R_{in} and R_{out}. These are treated microscopically (R_{in}, sec. 4) and as non-equilibrium polarization of a continuous medium (sec. 2), respectively. The resulting expression for R_{out} [1-4] contains the optical dielectric constant ϵ_{op} of the solvent. This quantity varies with the photon energy E at which optical electron transfer occurs because of dielectric dispersion of the solvent. The free energy R_{out} therefore is a function of E in contrast to the thermal case in which ϵ_{op} is a constant, e.g., $\epsilon_{op} = 1.77$ for water at 25°C. The dependence of R_{out} on E has significant implications which are examined in the present paper for the case of photoelectron emission by aqueous solutions in the 5 to 11.5 eV range [5].

2. FREE ENERGY OF OUTER-SPHERE REORGANIZATION WITH DIELECTRIC DISPERSION

The real and imaginary parts of the dielectric constant of a non-ideally transparent liquid are $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$, respectively. There, n is the refractive index and k the absorption coefficient of the medium. The displacement current in such a dielectric is proportional to the real part ϵ_1, and consequently the electronic polarization of the medium depends on ϵ_1 at the appropriate frequency in the optical range. The value of $n^2 - k^2$ must be taken at the photon energy E at which electron transfer occurs. Thus, electron transfer is caused by photon absorption, and the electronic polarization of the medium therefore responds to the change of ionic valence of the photoionized species in the same scale of time as photon absorption. The quantity $n^2 - k^2$ therefore must be substituted for the optical dielectric constant in the expression for R_{out}. Thus,

$$R_{out}(E) = [(n^2 - k^2)^{-1} - \epsilon_s^{-1}]e^2/2a, \tag{1}$$

where ϵ_s is the static dielectric constant of the solvent, e the electronic charge, and a the radius of the assumed spherical boundary between inner- and outer-sphere regions. The reduced and oxidized species (denoted respectively by the the subscripts r and o) have somewhat different cavity radii, and one sets $a = 2a_r a_o/(a_r + a_o)$ as is done for thermal electron transfer [6].

Figure 1 shows the effect of dielectric dispersion on $R_{out}(E)$ of eq. (1). Results are displayed as the variation of the ratio F of $R_{out}(E)$ at E to the value of $R_{out}(1.77)$ for $n^2 = 1.77$ and $k^2 = 0$ (water at 25°C). Values of n and k were taken from [7]. The shape of the curve in fig. 1 is accounted for by the effect of normal and anomalous dispersion (absorption bands at 8.2 and 10.0 eV). It is seen that $R_{out}(E)$ can be as low as 65 per cent of $R_{out}(1.77)$ and that $R_{out}(E)$ changes quite rapidly in rather narrow intervals of E. Figure 1 applies to pure water, and variations of F may be somewhat different for concentrated electrolytes, especially in the range of absorption bands of the

anion (charge transfer to the solvent). The variations of ϵ_s in (1) with electrolyte concentration are not significant since ϵ_s^{-1} for aqueous solutions is small in comparison with $(n^2 - k^2)^{-1}$.

3. DETERMINATION OF THRESHOLD ENERGIES BY EXTRAPOLATION

Photoelectron emission by solutions is studied [5] by determining the number of electrons collected (on an electrode above the solution) per incident photon as a function of the photon energy E. The emission yield Y thus measured is proportional to the emission current density of theory [8] to a good measure under actual experimental conditions. It was shown [8] that Y is proportional to $(E - E_t)^p$, where E_t is the threshold energy of the species being photoionized and $p = 2$ or $5/2$. This relationship follows from a more general equation for Y under suitable simplifying conditions. The exponent $p = 2$ corresponds to the normal case in which image forces are taken into account at the solution-vacuum interface. The value $p = 5/2$ holds if one assumes that the image forces are negligible.

The threshold energy E_t is determined from a plot of $Y^{1/p}$ against E. This procedure was applied to water [9], inorganic anions [10] and cations [11], and weak acids and bases [12] in aqueous solution. It was found that the exponent $p = 5/2$ gave better fits to linear plots than $p = 2$ for species with $E_t < 8$ eV. Conversely, the exponent $p = 2$ was preferable to $5/2$ for $E_t \gtrsim 8$ eV. The statistical evidence for these values of p was fairly unambiguous in most cases, but the underlying reasons for the choice of $p = 5/2$ were mystifying. The absence of image forces is difficult to account for, and anyhow the magnitude of image forces would conceivably depend on the kinetic energy of mobile electrons in the liquid and not on the absolute value of the photon energy. These puzzling results are accounted for by the effect of dispersion on $R_{out}(E)$ as will now be shown.

The threshold energy is the sum of several contributions one of which is the free energy of outer-sphere reorganization R_{out} (sec. 4). Call E_t^0 the threshold energy at $Y = 0$ in the linear extrapolation plot of $Y^{1/p}$ against E. One has $R_{out} = R_{out}^0$ at $E = E_t^0$, and a different $R_{out}(E)$ at $E > E_t^0$. The value of E_t in $(E - E_t)^p$ therefore is not the constant E_t^0 but the quantity,

$$E_t = E_t^0 - [R_{out}^0 - R_{out}(E)], \tag{2}$$

depending on E. Since $R_{out}(E)$ may differ from R_{out}^0 by several tenths of electronvolt, plots of $Y^{1/p}$ against E are distorted.

Variations of $(E - E_t)^2$ with $E - E_t^0$ are shown in Fig. 2 for $E_t^0 = 6$ and 8 eV, respectively. Values of $E - E_t$ were calculated from fig. 1 and the values of $R_{out}^0 = 1.02$ and 0.81 eV at $E_t^0 = 6$ and 8 eV, respectively. These values of R_{out}^0 correspond to the typical case of $R_{out}(1.77) = 1.15$ eV for the cations of sec. 4. The curve $(E - E_t)^2$ vs. $(E - E_t^0)$ for $E_t^0 = 6$ eV in Fig. 2 is quite close to the points representing $(E - E_t^0)^{5/2}$. This result follows directly from Fig. 1. The ratio F decreases quite rapidly with increasing E in the 6 to 7.6 eV range, and consequently $(E - E_t)^2$ increases more rapidly than $(E - E_t^0)^2$. Conversely, the curve $(E - E_t)^2$ vs. $E - E_t^0$ for $E_t^0 = 8$ eV in Fig. 2 is fairly close to the quadratic dependence $(E - E_t^0)^2$ because the decrease of F between $E = 8.6$ and 9.4 eV is less pronounced than the variations of F for $E_t^0 = 6$ eV. Apparent variation of p from 5/2 to 2 for the results of Fig. 2 are solely due to the change of $R_{out}(E)$ with E as a result of dispersion. The statistical evidence in [10-12] upon which the choice of $p = 5/2$ was based therefore is misleading and does not provide any proof that the $(E - E_t)^{5/2}$ relationship is in fact observed. A more elaborate analysis must be developed on the basis of the quadratic dependence regardless of photon energy and with consideration of the variations of $R_{out}(E)$ with photon energy.
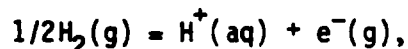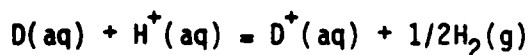
4. CALCULATED FREE ENERGIES OF EMISSION VERSUS EXPERIMENTAL THRESHOLD ENERGIES

The free energy ΔG_m for photoelectron emission by an aqueous solution of a donor D(aq) is [5,11]

$$\Delta G_m = \Delta G_H + \Delta G + R + |e|\Delta x . \tag{3}$$

There, ΔG_H and ΔG are the changes of free energy for the reactions,

$$D(aq) + H^+(aq) = D^+(aq) + 1/2H_2(g)$$

$$1/2H_2(g) = H^+(aq) + e^-(g),$$

respectively; R is the reorganization free energy taken as a <u>positive</u> quantity
for convenience; and Δx is the difference between the surface potentials $x[D(aq)]$
of the solution of $D(aq)$ and $x(H_2O)$ of water.

One has [13] $\Delta G_H = 4.48\pm0.05$ eV on the basis of a current determination
[14] of the real free energy of hydration (-11.25 eV) of the proton. This value
of ΔG_H includes the contribution of the surface potential $x(H_2O)$ of water.
The latter cannot be measured but can be estimated (0.08±0.06 eV [15]). The
surface potential $x[D(aq)]$ is generally different from that of water, and the
experimentally measurable [15] difference Δx therefore appears in (3). Since the
surface potential pertains to the change of potential from the liquid to vacuum,
a positive value of Δx corresponds to a higher barrier to emission than for $\Delta x = 0$. Hence, the quantity $|e|\Delta x$ in (3) is preceded by a positive sign. The
correction is quite minor anyhow since $|e|\Delta x$ is in general smaller than 0.05 to
0.1 eV in absolute value [15].

The reorganization free energy is $R = R_{out}(E) + R_{in}$, where R_{in} is
computed from the bond-stretching model used for thermal electron transfer [1].
Thus,

$$R_{in} = (N/2)f(\Delta q_0)^2, \tag{4}$$

where N is the number of ligands of the donor $D(aq)$; Δq_0 is the change of
equilibrium positions for vibration from the reduced species $D(aq)$ to $D^+(aq)$;
and f is the reduced force constant [6],

$$f = 2f_r f_0/(f_r + f_0). \tag{5}$$

Equation (4) gives an energy and not a free energy [1,6], but the resulting error
can be neglected since the model upon which eq. (4) is based is somewhat
simplified for hexaquo ions, for instance.

The f-values from [16] previously used [4] were computed from a Urey-Bradley potential in [17]. This gives f-values which are definitely too low, as was pointed out [18] to the writer, and experimental force constants must be used. One has [6],

$$f_r = 4\pi^2 \nu_r^2 c^2 \mu, \tag{6}$$

where ν_r is the stretching frequency (in cm^{-1}) and μ the reduced mass. A similar equation applies to f_0. Two limiting cases have been considered for μ in the case of hexaquo ions discussed below: (i) μ is set equal to the mass of a single water molecule m_{H_2O} [6,19]; (ii) $\mu = m_{H_2O} m_M / (m_{H_2O} + m_M)$, where m_M is the atomic mass of $M^{2+/3\ddagger}$ [20]. Method (i) slightly overestimates μ. Method (ii) certainly underestimates μ (by $\approx$ 20 to 25 per cent for the cations considered here) since it presupposes vibration between a "dry" cation $M^{2+/3+}$ and a water molecule. The first method was applied here. In the case of $Fe(CN)_6^{4-/3-}$, μ was set equal to the CN mass.

The Δq_0's in (4) computed from crystallographic metal-ligand distances from X-ray diffraction [6,19,20] generally agree with the Δq_0's recently determined by EXAFS for solutions [19]. The Δq_0 for $Fe(CN)_6^{4-/3-}$ is particularly low: 0.026 Å (crystallographic) vs. 0.01 Å (EXAFS, solutions) [19]. The calculation of R_{in} is sensitive to Δq_0, and an error of ± 0.01 Å on this quantity affects R_{in} by $\approx \pm 0.1$ to ± 0.15 eV for the cations discussed below.

Values of ΔG_m computed from eq. (3) are listed in Table 1 with the corresponding E_t's. Agreement can be considered to be good except for Fe^{2+} for an a priori (no data from emission) calculation of ΔG_m in view of the uncertainties on calculated R_{in}'s and extrapolated E_t's. The agreement for $Fe(CN)_6^{4-}$ shows that the threshold energy (5.7 eV) can be assigned to a direct bound-continuum transition. The threshold was attributed to autoionization of a bound state in [23] on the basis of the low value of E_t = 5.5 eV (obtained by extrapolation with p = 5/2) and a higher R_{in} value from

[16]. Assignment of emission autoionization bands [23], in general, will have to
be reexamined in the light of the present work. The discrepancy for Fe^{2+} is
ascribed mostly to the high E_t's (for $p = 5/2$ and $p = 2$) in Table 1 rather than
the calculated R_{in}. The latter indeed agrees well with the value $R_{in} = 0.69$
eV computed from experimental data on thermal electron transfer in sec. 5. Such
a calculation from kinetic data is reliable for $Fe^{2+/3+}$ [6].

5. CORRELATION BETWEEN OPTICAL AND THERMAL ELECTRON TRANSFER

Optical and thermal electron transfer were correlated in [4] without
consideration of dielectric dispersion. It was shown that the outer-sphere
reorganization free energy R_{out}^X for electron exchange (e.g., between Fe^{2+}
and Fe^{3+}) is practically the same as R_{out} for photoelectron emission. The
inner-sphere term R_{in}^X for exchange is twice R_{in} for emission since two
ions are involved in exchange and only one in emission. Thus, $R_{out}^X = R_{out}$
and $R_{in}^X = 2R_{in}$, and the reorganization free energy for exchange is $R^X =$
$R + R_{in}$. The effect of dielectric dispersion will now be considered.

The quantity R_{out}^X for exchange is generally computed for $\epsilon_{op} = 1.77$
for dilute aqueous solutions at 25°C, that is, $R_{out}^X = R_{out}(1.77)$. Hence,

$$R^X = R + R_{in} + \Delta R_{out}, \tag{7}$$

where the correction for dispersion is $\Delta R_{out} = R_{out}(1.77) - R_{out}(E)$,
$R_{out}(E)$ being computed at $E = E_t$. The free energy of activation $\Delta G^{\neq}$ for
electron exchange without net change of free energy is [1-3], $\Delta G^{\neq} = w + R^X/4$,
where w is the work required to bring from infinity in solution the two reactants
together in the activated complex.

Values of $\Delta G^{\neq}$ from (7) are listed in Table 2 with experimental values taken
from [1]. This comparison, it must be stressed, is only tentative because
calculated values of $\Delta G^{\neq}$ should be compared with the activation free energy for
electron transfer within the precursor complex [6]. Data are included only for
couples for which $\Delta G^{\neq}$ can be computed reasonably well from $\Delta G^{\neq} = R^X/4 + w$
[1-3]. Thus, exchange for $Co^{2+/3+}$ is known to be anomalously slow [19]. The

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"experimental" value $\Delta G^{\neq} = 0.75$ eV for $Mn^{2+/3+}$ obtained in [1] from the
Marcus cross relationship differs markedly from the value $\Delta G^{\neq} = 1.06$ eV
computed from R^X. Experimental (0.47 eV [1]) and calculated (0.31 eV) $\Delta G^{\neq}$'s
for $Fe(CN)_6^{4-/3-}$ also disagree.

Discrepancies in Table 2 can be interpreted on the basis of values of R_{in}
computed from $\Delta G^{\neq} = R^X/4 + w$ [1-3] by using the experimental $\Delta G^{\neq}$'s in Table 2
and calculated values of R_{out}^X ($= R_{out}(1.77)$). Errors on $\Delta G^{\neq}$ and R_{out}^X affect
the value of R_{in}, and application of the equation for $\Delta G^{\neq}$ is assumed to be
justified. Values of R_{in} thus obtained obviously must be viewed with caution.
One has $R_{in} = 1.09, 1.39, 0.69$ eV for V^{2+}, Cr^{2+}, Fe^{2+}, respectively, vs. 1.41,
1.27, 0.73 eV in Table 1. One concludes that the main source of discrepancy
between calculated and experimental $\Delta G^{\neq}$'s in Table 2 is mostly the high R_{in} of
Table 1 for $V^{2+/3+}$ and the high E_t (and consequently high R) for $Fe^{2+/3+}$.
Agreement for $Cr^{2+/3+}$ is reasonable.

In conclusion, consideration of dispersion is essential in future
determinations of experimental threshold energies. Free energies of emission
computed from data independent of emission generally agree with available
threshold energies within extrapolation error. Correlation between optical and
thermal electron transfer provides, whenever feasible, further verification of
the self-consistency of all data.

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Table 1

Calculated free energies of emission vs. experimental threshold energies.

	ΔG (eV)	R_{out} [a] (eV)	R_{in} [b] (eV)	ΔG_m (eV)	E_t [c] (eV)
V^{2+}	-0.25	0.99	1.41	6.63	6.38 (p=5/2)
					6.74 (p=2)
Cr^{2+}	-0.41	1.01	1.27	6.35	6.14 (p=5/2)
					6.51 (p=2)
Mn^{2+}	1.56	0.95	1.51	8.50	8.08 (p=2)
Fe^{2+}	0.77	0.93	0.73	6.91	7.35 (p=5/2)
					7.47 (p=2)
Co^{2+}	1.84	0.95	1.63	8.90	8.60 (p=2)
$Fe(CN)_6^{4-}$	0.36	0.77	0.06	5.67	5.5 (p=5/2)
					5.7 (p=2)

[a] From $FR_{out}(1.77)$ with F at E = ΔG_m (Fig. 1).   Values of $R_{out}(1.77)$ computed, respectively, for a = 3.48, 3.48, 3.56, 3.51, 3.48 Å from a_r and a_0 in [21] and a = 4.65 Å from [16].

[b] Calculated for N = 6; f = 1.7 x 10^5 dyne cm^{-1} for Cr^{2+} [19]; f from ν_r = 389 cm^{-1} and ν_0 = 490 cm^{-1} for all other cations except ν_r = 395 cm^{-1} for Mn^{2+} [20,22]; f = 4.5 x 10^5 dyne cm^{-1} for $Fe(CN)_6^{4-}$ from ν_r = 585 cm^{-1} and ν_0 = 511 cm^{-1} from [20,22]; Δq_0 = 0.20 (Cr^{2+}), 0.14 (Fe^{2+}), 0.21 (Co^{2+}), 0.026 ($Fe(CN)_6^{4-}$) Å from [19] and 0.195 (V^{2+}), 0.2 (Mn^{2+}) Å from [20].

[c] First E_t for p = 5/2 for V^{2+}, Cr^{2+}, Fe^{2+}, $Fe(CN)_6^{4-}$. Second E_t from emission spectra used in [11] for all cations and [23] for $Fe(CN)_6^{4-}$, but for extrapolation with p = 2. Only extrapolation for p = 2 for Mn^{2+} and Co^{2+} [11].

Table 2

Calculated and experimental free energies of activation for electron exchange

	R [a] (eV)	ΔR_{out} [b] (eV)	w [c] (eV)	$\Delta G^{\neq}$ [d] (calculated) (eV)	$\Delta G^{\neq}$ [e] (experimental) (eV)
$V^{2+/3+}$	2.15 (p=5/2)	0.15	0.04	0.97 (p=5/2)	0.87
	2.51 (p=2)			1.06 (p=2)	
$Cr^{2+/3+}$	2.07 (p=5/2)	0.13	0.05	0.92 (p=5/2)	1.03
	2.44 (p=2)			1.01 (p=2)	
$Fe^{2+/3+}$	2.10 (p=5/2)	0.18	0.06	0.81 (p=5/2)	0.69
	2.22 (p=2)			0.84 (p=2)	

[a] From eq. (3) and data in Table 1.

[b] From R_{out} in Table 1 and the corresponding $R_{out}(1.77)$.

[c] From [4].

[d] For R_{in} in Table 1.

[e] From [1].

Captions to Figures

Fig. 1. Plot of the ratio F of the outer-sphere reorganization free energy $R_{out}(E)$ at the photon energy E to $R_{out}(1.77)$ computed for $n^2 = 1.77$ and $k^2 = 0$.

Fig. 2. Spectral response for emission $(E - E_t)^2$ with consideration of dispersion compared with the responses $(E - E_t^0)^2$ and $(E - E_t^0)^{5/2}$ without dispersion.
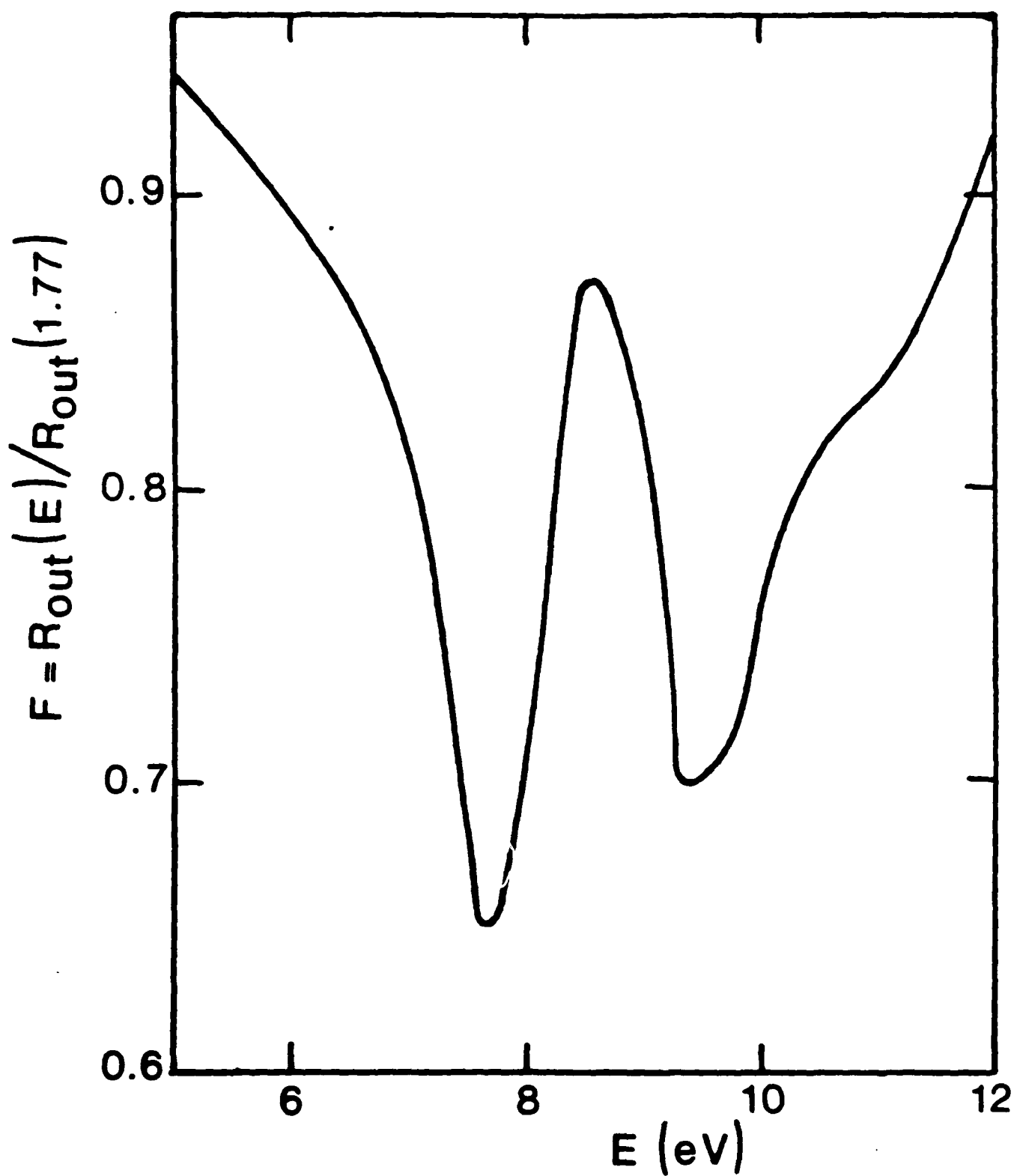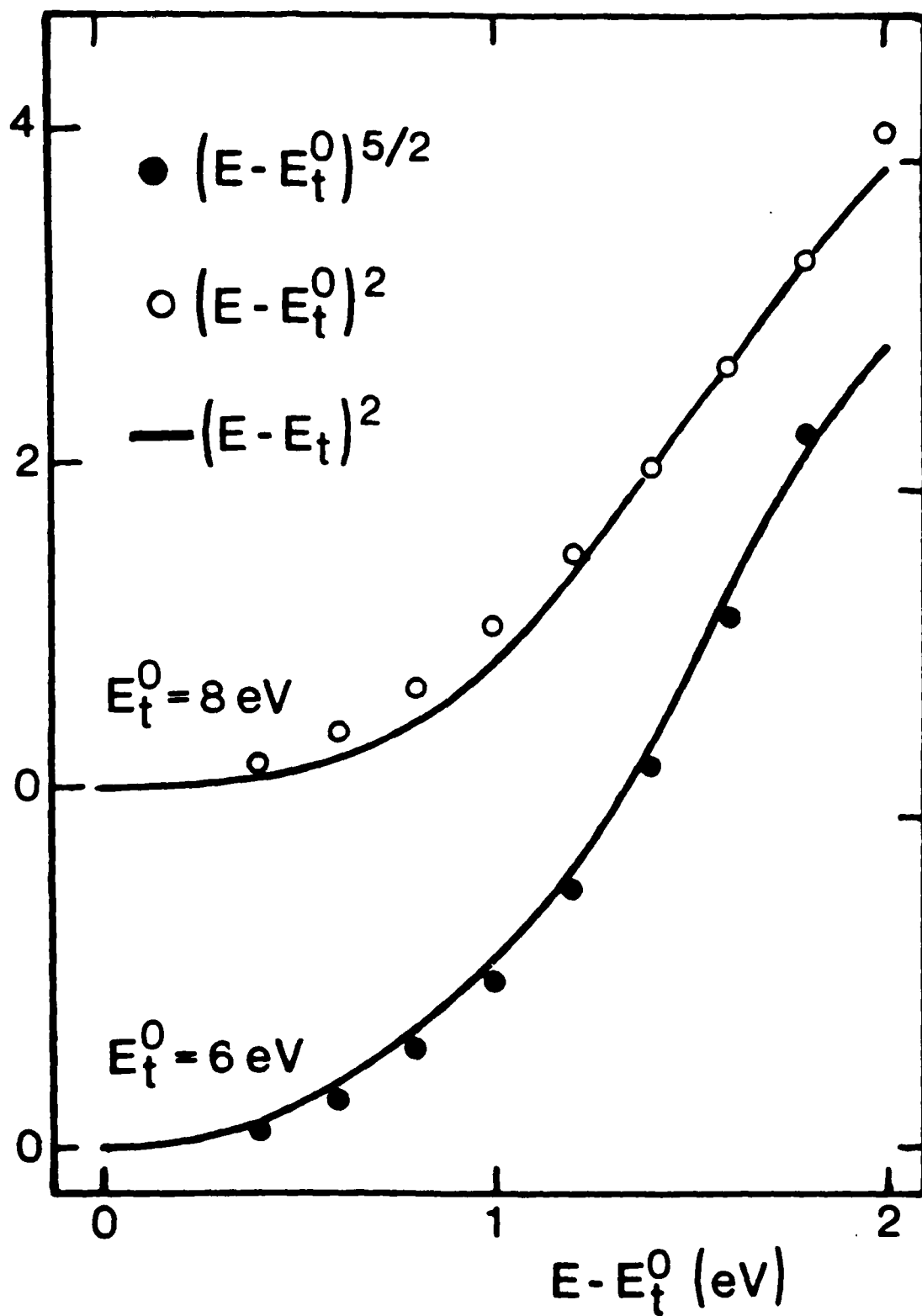
FIG. 1

FIG. 2

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